DESIGN OF LOW COST, HIGHLY ADSORBENT ACTIVATED CARBON FIBERS FOR AIR/WATER PURIFICATION

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13. ABSTRACT (Maximum 200 words)

U.S. troops face increasing risk of exposure to chemical and biological warfare threats as poorer nations and terrorist groups turn to these lower cost weapons for their arsenals. Despite the increased menace from these lethal agents, gas mask technology has remained virtually unchanged over the past several decades thus leaving soldiers at risk to newly developed nerve and pathogenic agents designed to defeat conventional GAC gas mask technology. EKOS Materials Corp. proposes a novel activated carbon fiber (ACF) that will combine the low cost and durability of GAC with tailored pore size and pore surface chemistry for improved defense against chemical weapons. One of the key advantages of this ACF is that it can be manufactured in a wide variety of product forms (textiles, felts, papers) which allows for vast design flexibility. Thus the potential exists to utilize carbon coated sub-micron glass fibers to replace both components of the current gas mask (HEPA filter and GAC) to greatly reduce pressure drop and achieve filtration/adsorption in a single step.

14. SUBJECT TERMS

activated carbon fibers; gas masks; adsorbents; chemical warfare; collective protection

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I. PROJECT OBJECTIVES AND SCHEDULE

The overall objective of the Phase I SBIR effort was to develop low cost activated carbon fibers (ACF) as a more effective adsorbent especially for removal of chemical warfare agents. As described in the Phase I proposal, work focused on synthesizing a variety of ACF samples for subsequent testing at the U.S. Army Edgewood RD&E Center. The PI traveled to Edgewood in mid-November to review the chemical and physical characteristics of the target contaminants, define size and potential configurations of the filter material, and establish testing protocols. Several batches of samples have been produced (Tasks 2&3) and tested using DMMP (isotherms) and cyanogen chloride (both isotherms and breakthrough tests) as discussed in Task 4. The results are very encouraging with adsorption effectiveness increased two-fold through tailoring of the pore size and pore surface chemistry of the carbon microstructure. One potential problem which has arisen is the high pressure drop across the fabrics. Attempts to utilize different filter configurations to address this problem resulted in poor retention of CK during breakthrough testing. Therefore, additional design work is required to minimize airflow resistance while retaining the necessary contact efficiency for rapid adsorption. Finally, the objective of Task 5 was to design a pilot scale furnace system that will be utilized in Phase II and subsequent work to provide increased capacity for preparation of ACF samples. This work was carried out by the sub-contractor Ceramic Composites Incorporated.

II. TECHNICAL PROGRESS
II.1 Design of Pilot Scale Processing System for ACFs

Current Activation Heating Schedules and Gas Flows

Preparation of the ACF material is currently performed in a tube furnace (3" or 4" diameter quartz tube). Activation of the phenolic coated glass mat is conducted in nitrogen at a temperature of 600°C. Initially the furnace is heated to 150°C with a nitrogen flow rate of 2 L/min. and held at that temperature for ~20 minutes. The temperature hold is to ensure oxygen and other potential reactants are removed from the tube prior to further heating. The fastest ramp rate possible to 600°C is used (6 - 10°C/min). If no other activation treatments are desired, then the furnace is shut off when it reaches 600°C and allowed to cool under flowing nitrogen.

Further activation treatment to modify the surface chemistry and/or increase porosity are performed at temperatures up to 900°C in various reactive atmospheres including steam, CO_2 and ammonia. The heating rate to 900°C is currently not controlled and dwell times at that temperature range from 1 - 2 hours. High gas flow rates are typically used to provide an excess of reactant. To produce the highly oxidized surface, the ACF was dipped into a solution of nitric acid and reacted for 60 minutes. The material is then washed several times with DI water to remove excess acid and dried at 150°C.

Current Capacity

The current tube furnaces are typically used to produce samples 1 - 2 sq. ft. in size. Larger samples 1' wide by 5' - 10' long have been made by rolling the sample mat prior to

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activation. Analysis of the pore character of samples taken from different regions of the rolled material (i.e., near the tube center vs. near the tube wall) were completed to determine if sufficiently uniform reactant gas/solid phase contact was achieved with the more productive rolled configuration. Pore size/distribution uniformity of these larger samples appears to be very dependent on flow rate and on their position relative to incoming reactant gases (higher surface areas are typically achieved on the influent side if flow rates are insufficient).

Pilot System Design Goals

The purpose of a pilot scale system is to enable EKOS to provide prospective customers (i.e., the US Army) with sample quantities sufficient for the full scale filter testing anticipated in Phase II. The pilot system should enable 2 - 10 times greater productivity than currently utilized methods. Activation runs currently take all day to complete, including furnace set up, heating schedule and cool down with lot sizes potentially ranging from 2 - 10 sq. ft.. Thus, the pilot scale system should have a capacity of 20 - 100 sq. ft. per day.

In order to reach these capacities and enable a variety of treatment conditions (i.e., activation temperatures and atmospheres) a laboratory scale "pusher" type furnace is proposed. Pusher furnace designs enable semi-continuous processing while maintaining atmosphere control. The basic element of the pusher furnace is the Inconel muffle, which serves as the air tight container in which the material is processed. For maximum temperature capability up to 1,100°C, the muffle is made of 600 series Inconel alloy. A schematic representation of the furnace design is shown in Figure 1 and discussed below.

Furnace Operation

The furnace will have an unheated entrance section for sample input, a heating zone in which the initial activation at 600°C in nitrogen and further activation to tailor pore size and surface chemistry are carried out, and a cooling section that will rapidly cool the samples to a temperature of nominally 100°C prior to removal into air. Each section of the three zone furnace will accommodate samples up to 12" in length and 4" wide and will have separate atmosphere control.

The entrance section will permit preheating up to a temperature of 150°C to remove any adsorbed moisture and purge any oxygen prior to entering the hot zone. This section will consist of a heavy duty, welded steel, leak proof muffle with air lock doors on either end and insulation to help maintain the desired temperature. Heating elements and/or preheated nitrogen gas flow will be used to control temperature. Thermocouples will provide feedback to the temperature controller for the entrance section.

The activation section will be maintained at the desired temperature (600 - 900°C) using nickel chrome alloy heating elements. These are relatively inexpensive and are the preferred heating element choice for maximum temperatures up to 1,100°C. Multiple thermocouples will be used to ensure an uniform temperature distribution. The activation section muffle will be made of welded Inconel 600 in a corrugated D-shaped design to resist warping from thermal

cycling. The muffle will have gas inlet ports and a vent port piped to a stack. Air lock doors on either end of the activation section muffle will enable transfer to and from this section.

Transfer from the entrance section to the activation section will be accomplished by slightly over pressuring the activation section with nitrogen (i.e., by closing the vent valve), opening the air lock door and manually pushing the sample carrier from the entrance section into the activation section using a push rod. Once the air lock door is closed, the activation gas vent valve is opened and the desired activation gas is flowed into the section. As activation of the first sample is being performed, a second sample is loaded into the entrance section for preheating.

Initial activation is performed at 600°C for about 1 hour. If additional treatment is desired, the temperature of the activation section can be ramped up and a different activating gas can be used. The activation section will be plumbed to accept 4 different gasses (e.g., nitrogen, ammonia, CO_2 and steam), each with its own mass flow controller. The heating element configuration will be designed to allow rapid heating (10°C per minute) within the activation temperature range (600 - 900°C). The use of low thermal mass insulation and air cooling around the muffle will enable rapid cooling within the activation temperature range.

Residence times in the activation chamber may range from 1 - 2.5 hours depending on the pore distribution and chemistry desired. Transfer to the cooling section will be accomplished by first purging the cooling section with nitrogen to ensure a non-oxidizing atmosphere. The activation gas vent valve will be closed and the air lock door between the activation section and the cooling section will be opened. The sample carrier will be pulled from the activation section into the cooling section using the pull rod. Positive pressure in both the activation section and the cooling section will prevent air from entering the chambers during transfer.

The cooling section muffle will be similar to the entrance section muffle but will be actively cooled by air cooling and/or a water jacket. The cooling section will not utilize insulation nor heating elements. A temperature probe with readout will indicate the sample temperature. The samples will be cooled to below 100°C prior to opening the door to minimize the risk of oxidation upon removal.

Processing Rates

The throughput of the furnace is limited by the required residence time in the activation section. Assuming activation times in the 1 - 2.5 hour range, a 12 hour processing day would allow completion of 4 - 10 sample sets, each with a different activation process, if desired.

Cost Estimate

Two furnace suppliers have been contacted and are preparing estimates for construction of the basic three zone furnace described here. CM Furnaces, Inc. (Bloomfield, NJ) and ThermCraft (Raleigh, NC) will be providing detailed quotes based on the specification provided. Ball park estimates fall in the $25,000 - $35,000 range including the structure, insulation, heating elements, thermocouples, temperature controllers and internal gas plumbing. Additional costs

will include external plumbing (for the water jacket), gas manifolds, mass flow controllers, and sample carriers, etc. are estimated to be in the $5,000 - $10,000 range.

II.2 Material Preparation

GAC is particularly disadvantaged for gas mask applications due to its slower adsorption kinetics and a pore surface chemistry which is acidic in nature (i.e. many chemical warfare gases are acidic or breakdown into acidic components). Therefore, the use of a fiber system with basic pores should greatly enhance adsorption efficiency. In addition, macro- and mesopore populations which dominate GAC surfaces hold adsorbents relatively weakly as compared to the micropores of the ACFs. For the low vapor pressure agents such as GB and VX, they can be effectively removed by physical adsorption processes, thus a large amount of micropore volume is required. However, high vapor pressure chemicals such as CK and phosgene typically require metal impregnants to breakdown these components. To avoid this expensive process, the focus of the Phase I program was determine the most effective pore size and surface chemistry for both types of contaminants.

As shown from previous results, the activation of phenolic based fibers with ammonia achieves a basic pore surface chemistry which is advantageous for removal of acidic gases (such as HCl). In addition, it was shown that the higher the nitrogen content, the higher the adsorption capacity. However, this higher nitrogen content is offset by an increase in the micropore size and surface area. Therefore, three samples were produced to give a range of pore sizes and nitrogen contents. Thus EKOS samples 24-6, 26-1, and 26-4 were produced through increasing activation time/temperature with ammonia and had nitrogen contents of 6.74, 11.7, and 9.6 weight percent, respectively. This should help to establish which variable was more important for removal of both high/low boiling point contaminants. Also, since the target molecules are polar in nature, a highly oxidized sample (surface rich in carboxylic acids and phenolic hydroxyls) was produced and tested to see if dipole-dipole interactions would increase adsorption efficiency (EKOS 26-3 with 18.9 weight percent acidic oxygen groups). Table I shows the physical characteristics of the samples produced through analysis of nitrogen adsorption isotherms. The values are reported for both the mat (carbon plus glass) and on a carbon basis as well. This allows for easier comparison especially since the amount of carbon can be controlled. Unfortunately, it was discovered that 26-4 as well as previous sample 26-5 did not follow the correct trend and were thus flawed (surface area of >1800 m^2/g expected). It appears that activation with ammonia at very high temperatures (needed to produce higher surface areas) is a detrimental process when using this type of glass substrate.

II.3 Adsorption Testing

As an initial screen of the ACF adsorbents to assess their viability for removal of chemical warfare agents, adsorption experiments with the high vapor pressure agent CK and a simulant for low vapor pressure agents, dimethyl methylphosphonate (DMMP) were carried out. CK has traditionally been very difficult to remove using traditional adsorbents and is typically used as a design-limiting agent to size chemical agent filters. DMMP has been

demonstrated to be an effective simulate for nerve agent GB. GB is generally used as the filter design-limiting agent for nerve agents and mustards because it possesses the highest vapor pressure of these classes of agents (thus it is the most weakly held).

DMMP Adsorption

Figures 2 and 3 show the adsorption isotherms for DMMP based on overall weight and on a carbon basis, respectively. This data was compared to a standard BPL carbon which is the precursor to ASZM-TEDA material used in gas masks. As expected, since DMMP is a high boiling point material, the most important parameter for removal is the available micropore volume. Therefore one notes a trend of increasing adsorption capacity as the micropore volume increases for both sets of data. The exception being sample 24-6 which showed poor performance with DMMP relative to its pore volume. This is due to a molecular sieving effect whereby the micropores are too small to accommodate a molecule the size of DMMP. This experiment was run twice to confirm the results. It is also interesting to note the flatness of the curve for 26-3. This is indicative of pore filling based on the stronger dipole interactions and thus one would expect a crossover with BPL at lower concentrations. In the case of DMMP, sample 26-1 adsorbs the highest capacity due to an increased micropore volume combined with a moderate pore size distribution. Thus the pores must be large enough to prohibit molecular sieving without greatly decreasing overlap potential.

CK Adsorption

For comparison, only the CK isotherms on a carbon weight basis are shown (Figure 4). As is obvious from the CK plot, the EKOS materials exhibit a substantially greater CK adsorption capacity at low partial pressures as compared to BPL carbon. And although sample 24-6 showed poor for adsorption for DMMP, it has the highest capacity for CK due to its small basic pores (the smaller pores have the higher overlap in potential thus holding onto the gaseous molecule more tightly while the basic functional group strongly enhance reaction with the slightly acidic character of the CK molecule). Thus, the EKOS materials should provide good retention of low boiling point vapors/gases which should aid in breakthrough performance. However it should be noted that the reactive capacity of the impregnated BPL type carbon used in military filters adds greatly to the amount of CK removed over that indicated in the plot for unimpregnated BPL. The larger pore samples have a smaller slope (and thus a higher adsorption energy) indicating that a crossover would occur at lower partial pressures. This indicates that the more basic ACFs are superior in the low regime (i.e. chemical effects dominate) but that a small pore is required to maintain that advantage as the concentration is increased.

CK Breakthrough Results

Due to limited quantities of ACF, the initial breakthrough experiments were conducted by adding two layers of the adsorbent at the outlet of a bed of the standard chemical warfare agent adsorbent, ASZM-TEDA carbon. The increased time for breakthrough then allows for calculation of the effectiveness of the ACF. Sample 26-1 could not be used due to fragility of the mat since it consisted of short, chopped silica fibers. For future samples, we will obtain a much

longer fiber (>1 inch) to give the mat good mechanical integrity. The testing conditions used for the CK breakthrough experiments were as follows (simulates JSGPM):

Adsorbent Bed Depths:
    ASZM-TEDA Carbon: 1.8 cm
    EKOS adsorbents: 0.1 cm
Air velocity: 4.63 cm/sec
CK feed conc.   4000 mg/m^3
Relative Humidity   80%
Temperature: 25C
Flow rate: 3.67 lpm

Utilization of EKOS samples 26-3 and 26-4 did not add a distinguishable amount of time to breakthrough (curves not shown for brevity). It is surprising that 26-3 did not extend the breakthrough time since it had increased CK adsorption as indicated in Figure 4. Since this sample was highly oxidized, it contained a large amount of chemical functional groups in the pores. Therefore the kinetics of adsorption may have decreased if adsorption requires a more site specific mechanism than pure physical adsorption (van der Waals), that is, the CK may not be effectively adsorbed until it locates a group to "bind" with. Another possibility is that the addition of so many groups onto the pore walls could result in constriction, whereby the pores are effectively smaller. Also, in the case of surface diffusion, the presence of numerous chemical group could interfere with the movement of molecules along the pore walls. One interesting possibility is that the strong acid groups present on the surface result in a chemical breakdown of CK (a fairly neutral molecule) into stronger acidic components. This would then allow for a significant advantage to be achieved when using the ammonia activated fibers with high nitrogen contents. Another critical aspect is to take into account the difference between laboratory and actual use conditions. The current challenge testing is done at much higher concentrations than are encountered in the field in order to reduce experimental time. The CK breakthrough is done at a concentration equal to 161 Pascals (Figure 4 indicates that only 26-4 has significant adsorption advantage over BPL at this concentration), however if the concentration is much lower, one notes that all of the EKOS samples should perform well.

The most encouraging data set comes from sample 24-6 as shown in the breakthrough curve Figure 5. Here we note a significant increase in time to breakthrough which correlates well with the data in Figure 4 where 24-6 adsorbs the highest capacity of CK. Calculations based on bed thickness indicate that this ACF is twice as effective for CK removal compared to the current ASZM-TEDA carbon. Two additional breakthrough experiments were also carried out with the 24-6 carbon coated glass. The first employed a spiral wound configuration in order to reduce the pressure drop, this resulted in almost immediate CK penetration. The second consisted of utilizing 40 layers of ACF (and no ASZM-TEDA carbon) compared to BPL carbon and the standard gas mask material. The curves are reproduced in Figure 6 which unfortunately shows very short breakthrough times for the ACF filter. The most likely reason for this behavior is "short circuiting" whereby the contaminant molecules are passing through holes in the fiber mat without coming into contact with the carbon. To remedy this problem, different types of fiber weaves and configurations will need to be considered in Phase II.

Pressure Drop

The airflow resistance was measured at a velocity of 4.63 cm/sec through the EKOS fiber mats. The typical value was 0.10 cm of water for two layers, compared to BPL carbon (12x30 mesh) an equivalent bed thickness would have a pressure drop of only 0.02 cm of water. This can be explained due to the high external surface of the small fibers. In contrast, the spiral wound adsorbent provided a substantial airflow resistance benefit over the 12x30 mesh GAC adsorbent currently used in NBC filters. The pressure drop was determined to be about 1 Pascal per mm of thickness, which is approximately one-half that of GAC. This type of airflow resistance would be very beneficial in protective mask applications to allow for ease of breathing. However, the same mechanism (channeling between adsorbent layers) which resulted in poor retention of CK challenge may also be responsible for the low airflow resistance. One of the most important trade-offs in selecting adsorbents for filter design is balancing the airflow resistance with mass transfer kinetics. Fortunately, the ACF has the advantage that it can be produced in a wide variety of products forms which allow for vast design flexibility.

SUMMARY

The Phase I data obtained on adsorption of CK and DMMP indicate that modification of the micropores can be an effective method for increasing capacity. Thus, the advantages offered by the EKOS fibers include (1) rapid mass transfer offered by the small diameter fibers and good contact efficiency, (2) ability to modify the pore size/chemistry, (3) immobilized nature of the adsorbent that avoids settling problems associated with granules. However, the disadvantages of relatively high airflow resistance and poor breakthrough characteristics will need to be addressed. Solving these problems will require further design of the ACF filter matrix which is an integral part of the Phase II program. One interesting aspect which has not been explored is the utilization of the ACF for aerosol collection. If the ACF cartridge could effectively remove both particulates and chemical warfare gases in a single step, a great savings in weight/volume could be achieved.

The Contractor, EKOS Materials Corp., hereby declares that, to the best of its knowledge and belief, the technical data delivered herewith under Contract No. DAAH01-99-C-R017 is complete, accurate, and complies with all requirements of the contract.

Date   June 24, 1999

Name and Title of Authorized Official   Christian J. Mangun - President

TABLE I: SURFACE AREA AND PORE STRUCTURE OF EKOS ADSORBENTS

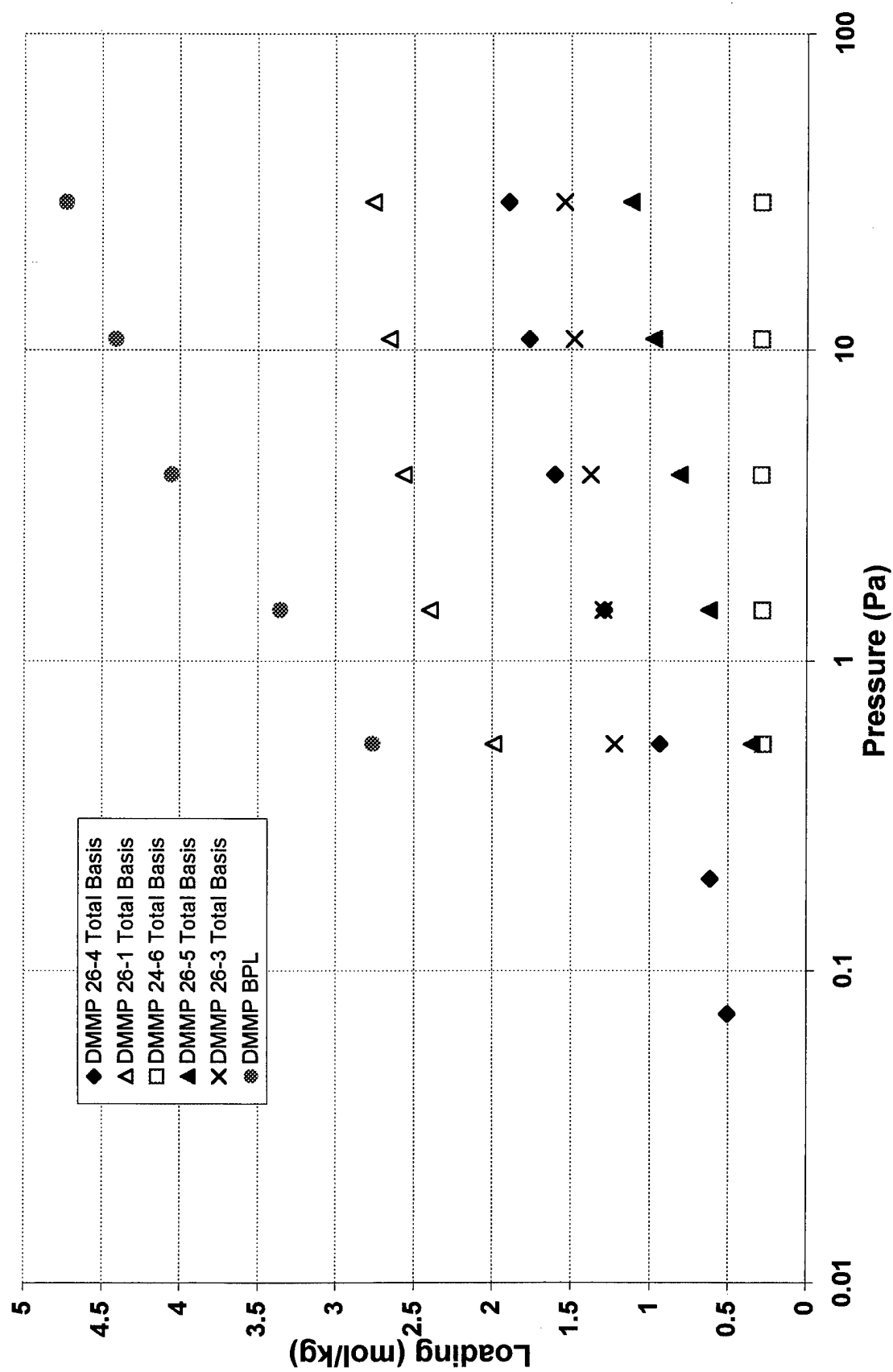| ADSORBENT	SURFACE AREA (MULTIPOINT BET)		TOTAL PORE VOLUME		MICROPORE VOLUME (t-METHOD)		PORE DIA AVERAGE
	M²/G MAT	M²/G CAR	CM³/G MAT	CM³/G CAR	CM³/G MAT	CM³/G CAR	ANGSTROMS
EKOS 24-6 (57.1% C)	362	634	0.266	0.466	0.181	0.317	29.3
EKOS 26-1 (53% C)	772	1457	0.466	0.879	0.392	0.740	24.1
EKOS 26-3 (61.5% C)	557	906	0.344	0.559	0.270	0.439	24.7
EKOS 26-4 (40.9% C)	598	1462	0.372	0.910	0.325	0.796	24.9
EKOS 26-5 (29.2% C)	247	846	0.213	0.729	0.187	0.640	34.4
BPL	1230	NA	0.681	NA	0.509	NA	22.2
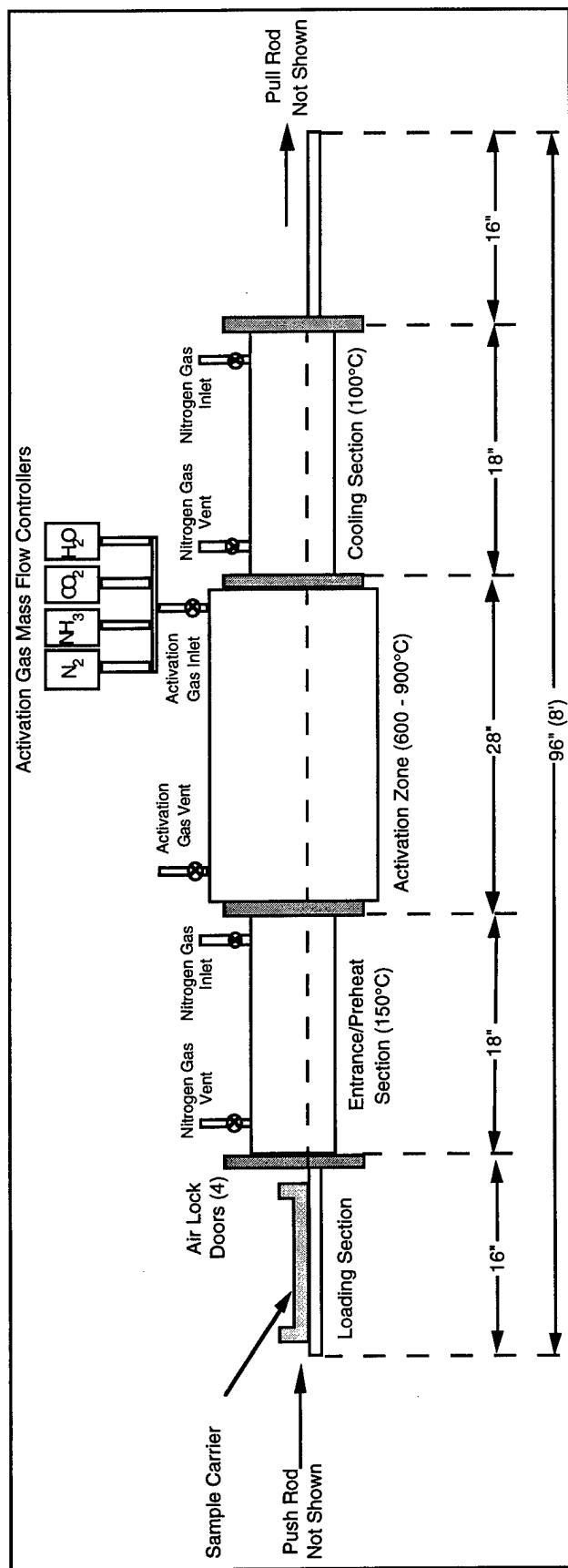
Figure 1. Schematic of three zone pusher furnace for processing of activated carbon fiber.

Figure 2: DMMP Adsorption Isotherm at 25C on Total Basis

Legend:
- ◆ DMMP 26-4 Total Basis
- △ DMMP 26-1 Total Basis
- ☐ DMMP 24-6 Total Basis
- ▲ DMMP 26-5 Total Basis
- ✕ DMMP 26-3 Total Basis
- ⬤ DMMP BPL

X-axis: Pressure (Pa)

Y-axis: Loading (mol/kg)

Figure 3: DMMP Adsorption Isotherm at 25C on Carbon Basis
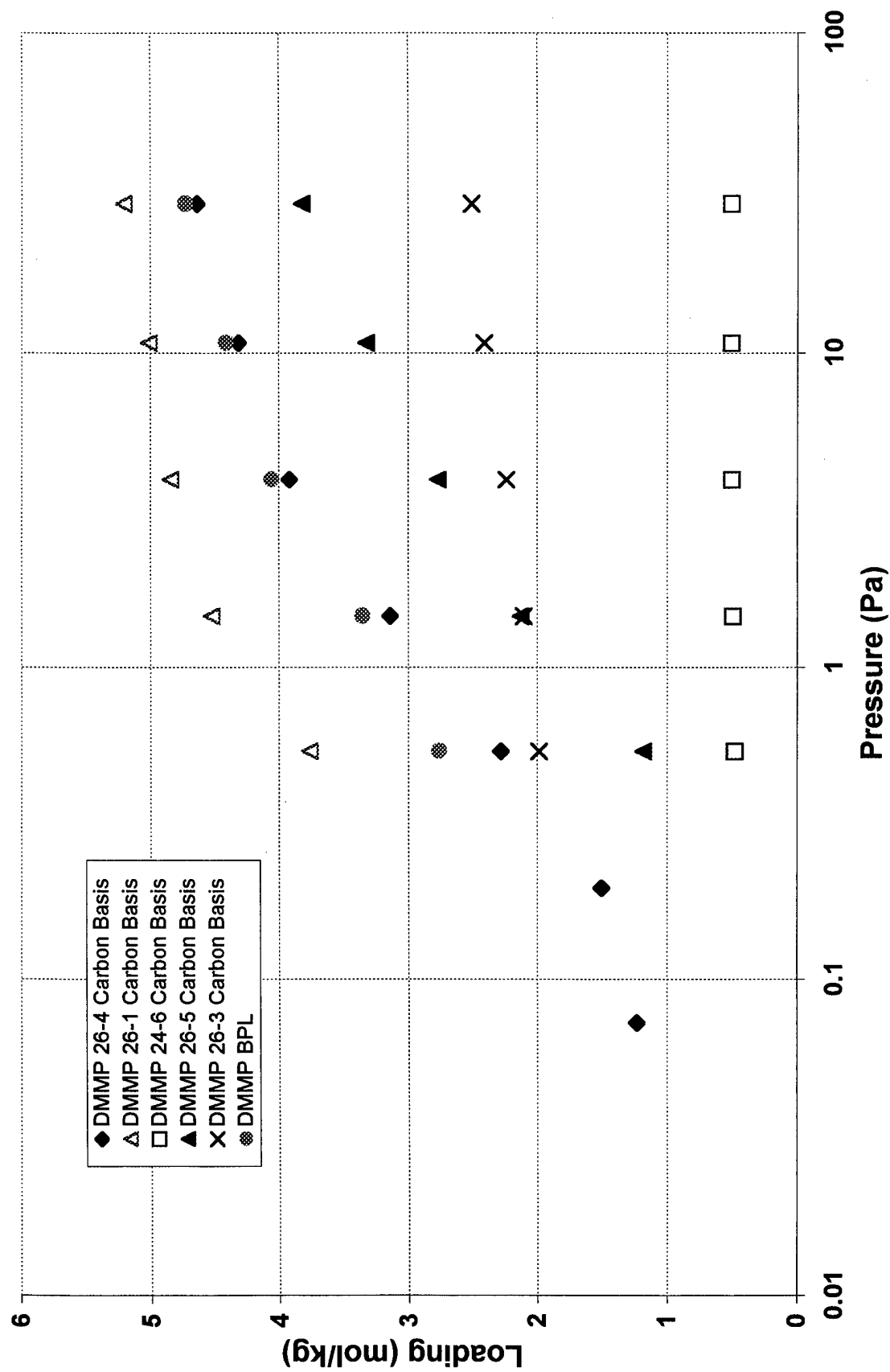
Figure 4: Cyanogen Chloride Adsorption Isotherm 25C Carbon Basis
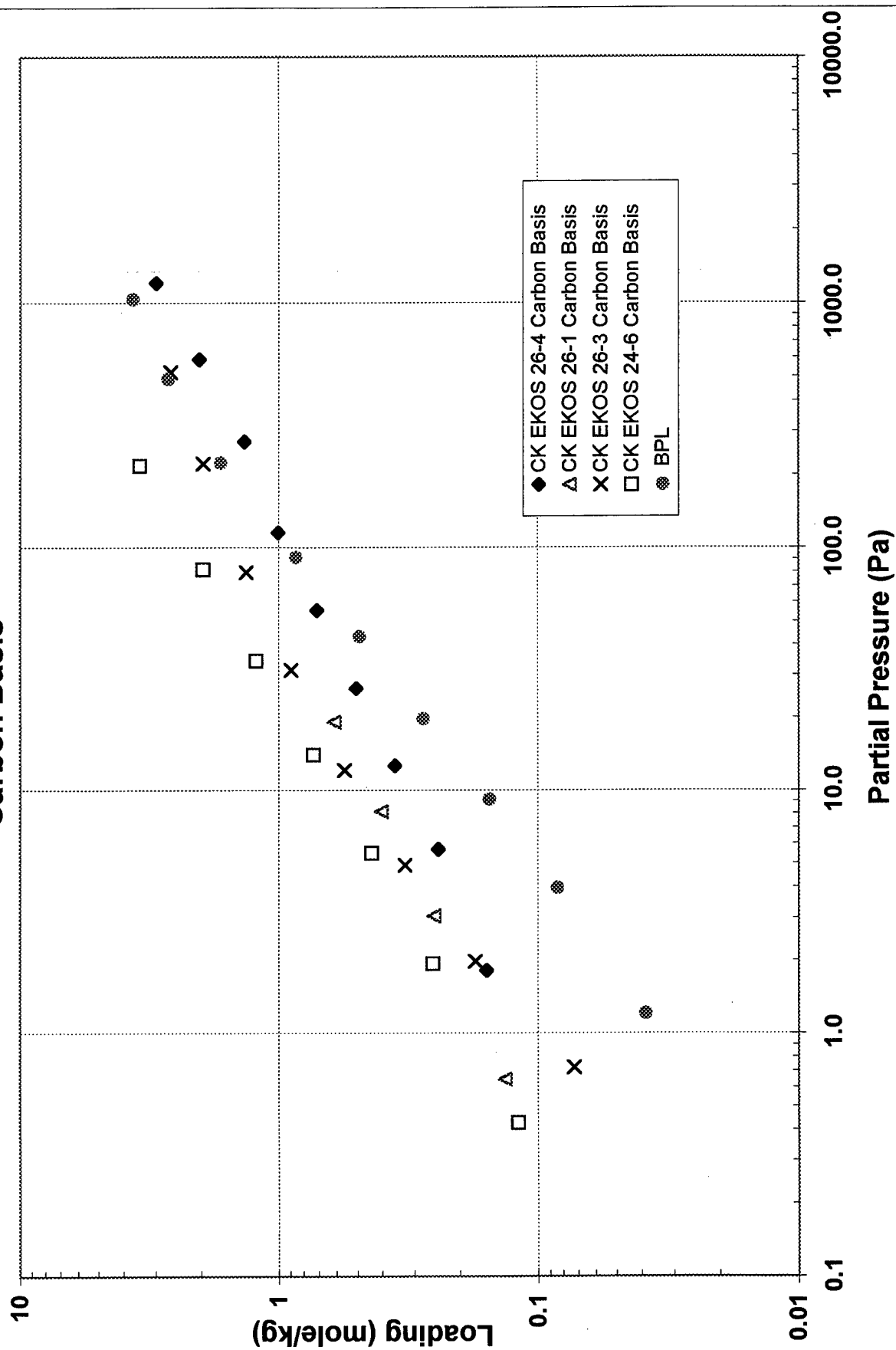
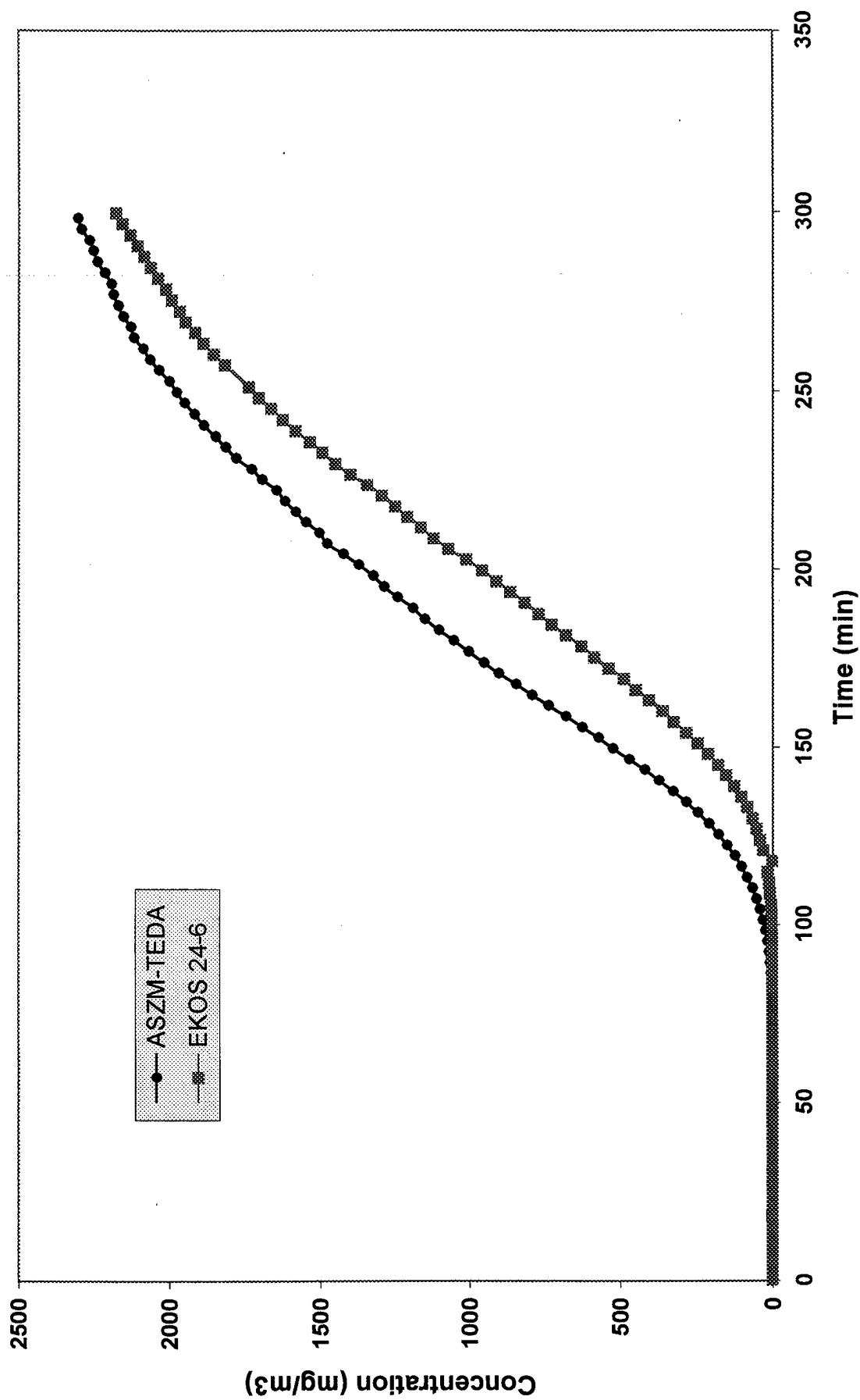Figure 5: CK Breakthrough Curve using Two Layers of EKOS 24-6

Figure 6: Humid CK Breakthrough of 40 Layers of EKOS 24-6 Adsorbent